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(54) Title: COMPOSITION AND METHOD FOR BLEACHING A SUBSTRATE

(57) Abstract: The invention relates to catalytically bleaching substrates, especially laundry fabrics, with atmospheric oxygen or air. A method of bleaching a substrate is provided that comprises applying to the substrate, in an aqueous medium, a specified ligand from a selected class which forms a complex with a transition metal, the complex catalysing bleaching of the substrate by atmospheric oxygen. Also provided is an aqueous bleaching composition substantially devoid of peroxygen bleach or a peroxy-based or -generating bleach system. Also provided is a method of treating a textile such as a laundry fabric whereby a complex catalyses bleaching of the textile by atmospheric oxygen after the treatment. The catalyst may be used in dry form, or in a liquor that is then dried, such as an aqueous spray-on fabric treatment fluid or a wash liquor for laundry cleaning, or a non-aqueous dry cleaning fluid or spray-on aerosol fluid. The method can confer cleaning benefits to the textile after the treatment. Also provided is a dry textile having a catalyst applied or deposited thereon, whereby bleaching by atmospheric oxygen is catalysed on the textile.

- 1 - .

COMPOSITION AND METHOD FOR BLEACHING A SUBSTRATE

## FIELD OF INVENTION

This invention relates to compositions and methods for  
5 catalytically bleaching substrates with atmospheric oxygen,  
more particularly using a defined class of ligand or complex  
as catalyst, and further relates to ligands and complexes  
useful in such compositions and methods. This invention also  
relates to a method of treating textiles, such as laundry  
10 fabrics, using the defined class of ligand or complex as  
catalyst, more specifically to a method whereby bleaching by  
atmospheric oxygen is catalysed after the treatment.

## BACKGROUND OF INVENTION

15 Peroxygen bleaches are well known for their ability to  
remove stains from substrates. Traditionally, the substrate  
is subjected to hydrogen peroxide, or to substances which  
can generate hydroperoxyl radicals, such as inorganic or  
organic peroxides. Generally, these systems must be  
20 activated. One method of activation is to employ wash  
temperatures of 60°C or higher. However, these high  
temperatures often lead to inefficient cleaning, and can  
also cause premature damage to the substrate.

25 A preferred approach to generating hydroperoxyl bleach  
radicals is the use of inorganic peroxides coupled with  
organic precursor compounds. These systems are employed for  
many commercial laundry powders. For example, various  
European systems are based on tetraacetyl ethylenediamine  
30 (TAED) as the organic precursor coupled with sodium

- 2 -

perborate or sodium percarbonate, whereas in the United States laundry bleach products are typically based on sodium nonanoyloxybenzenesulfonate (SNOBS) as the organic precursor coupled with sodium perborate.

5

Precursor systems are generally effective but still exhibit several disadvantages. For example, organic precursors are moderately sophisticated molecules requiring multi-step manufacturing processes resulting in high capital costs.

10 Also, precursor systems have large formulation space requirements so that a significant proportion of a laundry powder must be devoted to the bleach components, leaving less room for other active ingredients and complicating the development of concentrated powders. Moreover, precursor  
15 systems do not bleach very efficiently in countries where consumers have wash habits entailing low dosage, short wash times, cold temperatures and low wash liquor to substrate ratios.

20 Alternatively, or additionally, hydrogen peroxide and peroxy systems can be activated by bleach catalysts, such as by complexes of iron and the ligand N4Py (*i.e.* N, N-bis(pyridin-2-yl-methyl)-bis(pyridin-2-yl)methylamine) disclosed in WO95/34628, or the ligand Tpen (*i.e.* N, N, N',  
25 N'-tetra(pyridin-2-yl-methyl)ethylenediamine) disclosed in WO97/48787. According to these publications, molecular oxygen may be used as the oxidant as an alternative to peroxide generating systems. However, no role in catalysing bleaching by atmospheric oxygen in an aqueous medium is  
30 reported.

- 3 -

It has long been thought desirable to be able to use atmospheric oxygen (air) as the source for a bleaching species, as this would avoid the need for costly hydroperoxyl generating systems. Unfortunately, air as such is kinetically inert towards bleaching substrates and exhibits no bleaching ability. Recently some progress has been made in this area. For example, WO 97/38074 reports the use of air for oxidising stains on fabrics by bubbling air through an aqueous solution containing an aldehyde and a radical initiator. A broad range of aliphatic, aromatic and heterocyclic aldehydes is reported to be useful, particularly para-substituted aldehydes such as 4-methyl-, 4-ethyl- and 4-isopropyl benzaldehyde, whereas the range of initiators disclosed includes N-hydroxysuccinimide, various peroxides and transition metal coordination complexes.

However, although this system employs molecular oxygen from the air, the aldehyde component and radical initiators such as peroxides are consumed during the bleaching process. These components must therefore be included in the composition in relatively high amounts so as not to become depleted before completion of the bleaching process in the wash cycle. Moreover, the spent components represent a waste of resources as they can no longer participate in the bleaching process.

Accordingly, it would be desirable to be able to provide a bleaching system based on atmospheric oxygen or air that does not rely primarily on hydrogen peroxide or a hydroperoxyl generating system, and that does not require the presence of organic components such as aldehydes that

- 4 -

are consumed in the process. Moreover, it would be desirable to provide such a bleaching system that is effective in aqueous medium.

5 It may also be noted that the known art teaches a bleaching effect only as long as the substrate is being subjected to the bleaching treatment. Thus, there is no expectation that hydrogen peroxide or peroxy bleach systems could continue to provide a bleaching effect on a treated substrate, such as a  
10 laundry fabric after washing and drying, since the bleaching species themselves or any activators necessary for the bleaching systems would be assumed to be removed from the substrate, or consumed or deactivated, on completing the wash cycle and drying.

15 It would be therefore also be desirable to be able to treat a textile such that, after the treatment is completed, a bleaching effect is observed on the textile. Furthermore, it would be desirable to be able to provide a bleach  
20 treatment for textiles such as laundry fabrics whereby residual bleaching occurs when the treated fabric has been treated and is dry.

#### SUMMARY OF INVENTION

25 We have found that a selected class of ligand or complex as defined below is surprisingly effective in catalysing the bleaching of substrates using atmospheric oxygen or air. Furthermore, we have found certain novel ligands, which are useful in the bleaching of substrates using atmospheric  
30 oxygen or air.

- 5 -

Accordingly, in a first aspect, the present invention provides a bleaching composition comprising, in an aqueous medium, atmospheric oxygen and a ligand which forms a complex with a transition metal, the complex catalysing  
5 bleaching of a substrate by the atmospheric oxygen, wherein the aqueous medium is substantially devoid of peroxygen bleach or a peroxy-based or -generating bleach system. The medium is therefore preferably insensitive or stable to catalase, which acts on peroxy species.

10

In a second aspect, the present invention provides a method of bleaching a substrate comprising applying to the substrate, in an aqueous medium, a ligand which forms a complex with a transition metal, the complex catalysing  
15 bleaching of the substrate by atmospheric oxygen.

Furthermore, in a third aspect, the present invention provides the use of a ligand which forms a complex with a transition metal as a catalytic bleaching agent for a  
20 substrate in an aqueous medium substantially devoid of peroxygen bleach or a peroxy-based or -generating bleach system, the complex catalysing bleaching of the substrate by the atmospheric oxygen.

25 We have also found that certain ligands or complexes of this class are surprisingly effective in catalysing bleaching of the substrate by atmospheric oxygen after treatment of the substrate.

30 Accordingly, in a fourth aspect, the present invention provides a method of treating a textile by contacting the

- 6 -

textile with a ligand which forms a complex with a transition metal, whereby the complex catalyses bleaching of the textile by atmospheric oxygen after the treatment.

- 5 In a fifth aspect, the present invention provides a dry textile having a ligand as defined above applied or deposited thereon, whereby bleaching by atmospheric oxygen is catalysed on the textile.
- 10 In further aspects, the present invention provides ligands and complexes, as defined further below.

- Advantageously, the method according to the present invention permits all or the majority of the bleaching
- 15 species in the medium (on an equivalent weight basis) to be derived from atmospheric oxygen. Thus, the medium can be made wholly or substantially devoid of peroxygen bleach or a peroxy-based or -generating bleach system. Furthermore, the complex is a catalyst for the bleaching process and, as
- 20 such, is not consumed but can continue to participate in the bleaching process. The catalytically activated bleaching system of the type in accordance with the present invention, which is based on atmospheric oxygen, is therefore both cost-effective and environmentally friendly. Moreover, the
- 25 bleaching system is operable under unfavourable wash conditions which include low temperatures, short contact times and low dosage requirements. Furthermore, the method is effective in an aqueous medium and is therefore particularly applicable to bleaching of laundry fabrics.
- 30 Therefore, whilst the composition and method according to the present invention may be used for bleaching any suitable

- 7 -

substrate, the preferred substrate is a laundry fabric. The bleaching method may be carried out by simply leaving the substrate in contact with the medium for a sufficient period of time. Preferably, however, the aqueous medium on or  
5 containing the substrate is agitated.

An advantage of the method according to the fourth aspect of the invention is that, by enabling a bleaching effect even after the textile has been treated, the benefits of  
10 bleaching can be prolonged on the textile. Furthermore, since a bleaching effect is conferred to the textile after the treatment, the treatment itself, such as a laundry wash cycle, may for example be shortened. Moreover, since a bleaching effect is achieved by atmospheric oxygen after  
15 treatment of the textile, hydrogen peroxide or peroxy-based bleach systems can be omitted from the treatment substance.

The present invention also extends to a commercial package comprising a ligand or complex as defined below together  
20 with instructions for its use.

The present invention also extends to use of a ligand or complex as defined below in the manufacture of a bleaching composition, the bleaching composition substantially devoid  
25 of peroxygen bleach or a peroxy-based or peroxy-generating bleach system.

#### DETAILED DESCRIPTION OF THE INVENTION

The ligand may be present as a preformed complex of a ligand  
30 and a transition metal. Alternatively, the composition may comprise a free ligand that complexes with a transition



- 8 -

metal already present in the water or that complexes with a transition metal present in the substrate. The composition may also be formulated as a composition of a free ligand or a transition metal-substitutable metal-ligand complex, and a  
 5 source of transition metal, whereby the complex is formed *in situ* in the medium.

The ligand forms a complex with one or more transition metals, in the latter case for example as a dinuclear  
 10 complex. Suitable transition metals include for example: manganese in oxidation states II-V, iron II-V, copper I-III, cobalt I-III, titanium II-IV, tungsten IV-VI, vanadium II-V and molybdenum II-VI.

15 The ligand forms a complex of the general formula (A1):



in which:

20 M represents a metal selected from Mn(II)-(III)-(IV)-(V), Cu(I)-(II)-(III), Fe(II)-(III)-(IV)-(V), Co(I)-(II)-(III), Ti(II)-(III)-(IV), V(II)-(III)-(IV)-(V), Mo(II)-(III)-(IV)-(V)-(VI) and W(IV)-(V)-(VI), preferably selected from Fe(II)-(III)-(IV)-(V);

25 L represents a ligand as herein defined, or its protonated or deprotonated analogue;

X represents a coordinating species selected from any mono, bi or tri charged anions and any neutral molecules able to coordinate the metal in a mono, bi or tridentate  
 30 manner, preferably selected from  $O^{2-}$ ,  $RBO_2^{2-}$ ,  $RCOO^-$ ,  $RCONR^-$ ,  $OH^-$ ,  $NO_3^-$ ,  $NO$ ,  $S^{2-}$ ,  $RS^-$ ,  $PO_4^{3-}$ ,  $PO_3OR^{3-}$ ,  $H_2O$ ,  $CO_3^{2-}$ ,  $HCO_3^-$ ,  $ROH$ ,

- 9 -

$N(R)_3$ ,  $ROO^-$ ,  $O_2^{2-}$ ,  $O_2^-$ ,  $RCN$ ,  $Cl^-$ ,  $Br^-$ ,  $OCN^-$ ,  $SCN^-$ ,  $CN^-$ ,  $N_3^-$ ,  $F^-$ ,  
 $I^-$ ,  $RO^-$ ,  $ClO_4^-$ , and  $CF_3SO_3^-$ , and more preferably selected from  
 $O^{2-}$ ,  $RBO_2^{2-}$ ,  $RCOO^-$ ,  $OH^-$ ,  $NO_3^-$ ,  $S^{2-}$ ,  $RS^-$ ,  $PO_3^{4-}$ ,  $H_2O$ ,  $CO_3^{2-}$ ,  $HCO_3^-$ ,  
 $ROH$ ,  $N(R)_3$ ,  $Cl^-$ ,  $Br^-$ ,  $OCN^-$ ,  $SCN^-$ ,  $RCN$ ,  $N_3^-$ ,  $F^-$ ,  $I^-$ ,  $RO^-$ ,  $ClO_4^-$ ,  
5 and  $CF_3SO_3^-$ ;

Y represents any non-coordinated counter ion,  
preferably selected from  $ClO_4^-$ ,  $BR_4^-$ ,  $[MX_4]^-$ ,  $[MX_4]^{2-}$ ,  $PF_6^-$ ,  
 $RCOO^-$ ,  $NO_3^-$ ,  $RO^-$ ,  $N^+(R)_4$ ,  $ROO^-$ ,  $O_2^{2-}$ ,  $O_2^-$ ,  $Cl^-$ ,  $Br^-$ ,  $F^-$ ,  $I^-$ ,  
 $CF_3SO_3^-$ ,  $S_2O_6^{2-}$ ,  $OCN^-$ ,  $SCN^-$ ,  $H_2O$ ,  $RBO_2^{2-}$ ,  $BF_4^-$  and  $BPh_4^-$ , and  
10 more preferably selected from  $ClO_4^-$ ,  $BR_4^-$ ,  $[FeCl_4]^-$ ,  $PF_6^-$ ,  
 $RCOO^-$ ,  $NO_3^-$ ,  $RO^-$ ,  $N^+(R)_4$ ,  $Cl^-$ ,  $Br^-$ ,  $F^-$ ,  $I^-$ ,  $CF_3SO_3^-$ ,  $S_2O_6^{2-}$ ,  
 $OCN^-$ ,  $SCN^-$ ,  $H_2O$  and  $BF_4^-$ ;

a represents an integer from 1 to 10, preferably from 1  
to 4;

15 k represents an integer from 1 to 10;

n represents an integer from 1 to 10, preferably from 1  
to 4;

m represents zero or an integer from 1 to 20,  
preferably from 1 to 8; and

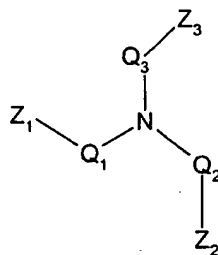
20 each R independently represents a group selected from  
hydrogen, hydroxyl,  $-R'$  and  $-OR'$ , wherein  $R'$  = alkyl, alkenyl,  
cycloalkyl, heterocycloalkyl, aryl, heteroaryl or a carbonyl  
derivative group,  $R'$  being optionally substituted by one or  
more functional groups E, wherein E independently represents  
25 a functional group selected from  $-F$ ,  $-Cl$ ,  $-Br$ ,  $-I$ ,  $-OH$ ,  $-OR'$ ,  
 $-NH_2$ ,  $-NHR'$ ,  $-N(R')_2$ ,  $-N(R')_3^+$ ,  $-C(O)R'$ ,  $-OC(O)R'$ ,  $-COOH$ ,  $-COO^-$   
 $(Na^+, K^+)$ ,  $-COOR'$ ,  $-C(O)NH_2$ ,  $-C(O)NHR'$ ,  $-C(O)N(R')_2$ ,  
heteroaryl,  $-R'$ ,  $-SR'$ ,  $-SH$ ,  $-P(R')_2$ ,  $-P(O)(R')_2$ ,  $-P(O)(OH)_2$ ,  
 $-P(O)(OR')_2$ ,  $-NO_2$ ,  $-SO_3H$ ,  $-SO_3^-(Na^+, K^+)$ ,  $-S(O)_2R'$ ,  $-NHC(O)R'$ , and  
30  $-N(R')C(O)R'$ , wherein  $R'$  represents cycloalkyl, aryl,

- 10 -

arylalkyl, or alkyl optionally substituted by -F, -Cl, -Br, -I, -NH<sub>3</sub><sup>+</sup>, -SO<sub>3</sub>H, -SO<sub>3</sub><sup>-</sup>(Na<sup>+</sup>, K<sup>+</sup>), -COOH, -COO<sup>-</sup>(Na<sup>+</sup>, K<sup>+</sup>), -P(O)(OH)<sub>2</sub>, or -P(O)(O<sup>-</sup>(Na<sup>+</sup>, K<sup>+</sup>))<sub>2</sub>, and preferably each R independently represents hydrogen, optionally substituted  
 5 alkyl or optionally substituted aryl, more preferably hydrogen or optionally substituted phenyl, naphthyl or C<sub>1-4</sub>-alkyl.

The ligand L is of the general formula (I):

10



(I)

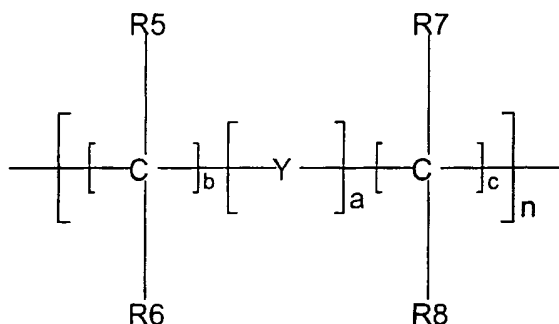
wherein

Z<sub>1</sub>, Z<sub>2</sub> and Z<sub>3</sub> independently represent a coordinating  
 15 group selected from carboxylate, amido, -NH-C(NH)NH<sub>2</sub>, hydroxyphenyl, an optionally substituted heterocyclic ring or an optionally substituted heteroaromatic ring selected from pyridine, pyrimidine, pyrazine, pyrazole, imidazole, benzimidazole, quinoline, quinoxaline, triazole,  
 20 isoquinoline, carbazole, indole, isoindole, oxazole and thiazole;

Q<sub>1</sub>, Q<sub>2</sub>, and Q<sub>3</sub> independently represent a group of the formula:

25

- 11 -



wherein

5         $5 \geq a+b+c \geq 1$ ;  $a=0-5$ ;  $b=0-5$ ;  $c=0-5$ ;  $n=1$  or  $2$ ;

Y independently represents a group selected from -O-, -S-, -SO-, -SO<sub>2</sub>-, -C(O)-, arylene, alkylene, heteroarylene, heterocycloalkylene, -(G)P-, -P(O)- and -(G)N-, wherein G  
 10 is selected from hydrogen, alkyl, aryl, arylalkyl, cycloalkyl, each except hydrogen being optionally substituted by one or more functional groups E; and

R5, R6, R7, R8 independently represent a group selected  
 15 from hydrogen, hydroxyl, halogen, -R and -OR, wherein R represents alkyl, alkenyl, cycloalkyl, heterocycloalkyl, aryl, heteroaryl or a carbonyl derivative group, R being optionally substituted by one or more functional groups E,  
 or R5 together with R6, or R7 together with R8, or  
 20 both, represent oxygen,

or R5 together with R7 and/or independently R6 together with R8, or R5 together with R8 and/or independently R6 together with R7, represent C<sub>1-6</sub>-alkylene optionally substituted by C<sub>1-4</sub>-alkyl, -F, -Cl, -Br or -I.

25

- 12 -

$Z_1$ ,  $Z_2$  and  $Z_3$  each represent a coordinating group, preferably selected from optionally substituted pyridin-2-yl, optionally substituted imidazol-2-yl, optionally substituted imidazol-4-yl, optionally substituted pyrazol-1-yl, and  
5 optionally substituted quinolin-2-yl. Preferably,  $Z_1$ ,  $Z_2$  and  $Z_3$  each represent optionally substituted pyridin-2-yl.

Optional substituents for the groups  $Z_1$ ,  $Z_2$  and  $Z_3$  are preferably selected from  $C_{1-4}$ -alkyl, aryl, arylalkyl,  
10 heteroaryl, methoxy, hydroxy, nitro, amino, carboxyl, halo, and carbonyl, preferably methyl.

The groups R5-R8 are preferably independently selected from -H, hydroxy- $C_0$ - $C_{20}$ -alkyl, halo- $C_0$ - $C_{20}$ -alkyl, nitroso, formyl-  
15  $C_0$ - $C_{20}$ -alkyl, carboxyl- $C_0$ - $C_{20}$ -alkyl and esters and salts thereof, carbamoyl- $C_0$ - $C_{20}$ -alkyl, sulfo- $C_0$ - $C_{20}$ -alkyl and esters and salts thereof, sulfamoyl- $C_0$ - $C_{20}$ -alkyl, amino- $C_0$ - $C_{20}$ -alkyl, aryl- $C_0$ - $C_{20}$ -alkyl,  $C_0$ - $C_{20}$ -alkyl, alkoxy- $C_0$ - $C_8$ -alkyl, carbonyl- $C_0$ - $C_6$ -alkoxy, and  $C_0$ - $C_{20}$ -alkylamide. Preferably, none of R5-  
20 R8 is linked together.

Also preferred is that  $Q_1$ ,  $Q_2$  and  $Q_3$  are defined such that  $a=b=0$ ,  $c=1$  or  $2$ , and  $n=1$ .

25 Preferably, each  $Q_1$ ,  $Q_2$  and  $Q_3$  independently represent  $C_{1-4}$ -alkylene, more preferably a group selected from  $-CH_2-$  and  $-CH_2CH_2-$ .

Preferably, the ligand L is selected from tris(pyridin-2-  
30 ylmethyl)amine, tris(3-methyl-pyridin-2-ylmethyl)amine, tris(5-methyl-pyridin-2-ylmethyl)amine, tris(4-t-butyl-

- 13 -

pyridin-2-ylmethyl)amine and tris(6-methyl-pyridin-2-ylmethyl)amine.

The counter ions Y in formula (A1) balance the charge z on  
5 the complex formed by the ligand L, metal M and coordinating species X. Thus, if the charge z is positive, Y may be an anion such as  $\text{RCOO}^-$ ,  $\text{BPh}_4^-$ ,  $\text{ClO}_4^-$ ,  $\text{BF}_4^-$ ,  $\text{PF}_6^-$ ,  $\text{RSO}_3^-$ ,  $\text{RSO}_4^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ , or  $\text{I}^-$ , with R being hydrogen, optionally substituted alkyl or optionally substituted aryl.  
10 If z is negative, Y may be a common cation such as an alkali metal, alkaline earth metal or (alkyl)ammonium cation.

Suitable counter ions Y include those which give rise to the formation of storage-stable solids. Preferred counter ions  
15 for the preferred metal complexes are selected from  $\text{R}^7\text{COO}^-$ ,  $\text{ClO}_4^-$ ,  $\text{BF}_4^-$ ,  $\text{PF}_6^-$ ,  $\text{RSO}_3^-$  (in particular  $\text{CF}_3\text{SO}_3^-$ ),  $\text{RSO}_4^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ , and  $\text{I}^-$ , wherein R represents hydrogen or optionally substituted phenyl, naphthyl or  $\text{C}_1\text{-C}_4$  alkyl.

20 It will be appreciated that the complex (A1) can be formed by any appropriate means, including *in situ* formation whereby precursors of the complex are transformed into the active complex of general formula (A1) under conditions of storage or use. Preferably, the complex is formed as a  
25 well-defined complex or in a solvent mixture comprising a salt of the metal M and the ligand L or ligand L-generating species. Alternatively, the catalyst may be formed *in situ* from suitable precursors for the complex, for example in a solution or dispersion containing the precursor materials.  
30 In one such example, the active catalyst may be formed *in situ* in a mixture comprising a salt of the metal M and the

- 14 -

ligand L, or a ligand L-generating species, in a suitable solvent. Thus, for example, if M is iron, an iron salt such as  $\text{FeSO}_4$  can be mixed in solution with the ligand L, or a ligand L-generating species, to form the active complex.

5 Thus, for example, the composition may be formed from a mixture of the ligand L and a metal salt  $\text{MX}_n$  in which preferably  $n=1-5$ , more preferably 1-3. In another such example, the ligand L, or a ligand L-generating species, can be mixed with metal M ions present in the substrate or wash liquor to form the  
10 active catalyst *in situ*. Suitable ligand L-generating species include metal-free compounds or metal coordination complexes that comprise the ligand L and can be substituted by metal M ions to form the active complex according to the formula (A1).

15

The bleaching compositions according to the present invention may be used for laundry cleaning, hard surface cleaning (including cleaning of lavatories, kitchen work surfaces, floors, mechanical ware washing etc.). As is  
20 generally known in the art, bleaching compositions are also employed in waste-water treatment, pulp bleaching during the manufacture of paper, leather manufacture, dye transfer inhibition, food processing, starch bleaching, sterilisation, whitening in oral hygiene preparations and/or  
25 contact lens disinfection.

In the context of the present invention bleaching should be understood as relating generally to the decolourisation of stains or of other materials attached to or associated with  
30 a substrate. However, it is envisaged that the present invention can be applied where a requirement is the removal

- 15 -

and/or neutralisation by an oxidative bleaching reaction of malodours or other undesirable components attached to or otherwise associated with a substrate. Furthermore, in the context of the present invention bleaching is to be understood as being restricted to any bleaching mechanism or process that does not require the presence of light or activation by light. Thus, photobleaching compositions and processes relying on the use of photobleach catalysts or photobleach activators and the presence of light are excluded from the present invention.

In typical washing compositions the level of the catalyst is such that the in-use level is from 0.05 $\mu$ M to 50mM, with preferred in-use levels for domestic laundry operations falling in the range 0.5  $\mu$ M to 100  $\mu$ M, more preferably from 1  $\mu$ M to 10  $\mu$ M. Higher levels may be desired and applied in industrial bleaching processes, such as textile and paper pulp bleaching.

Preferably, the aqueous medium has a pH in the range from pH 6 to 13, more preferably from pH 6 to 11, still more preferably from pH 8 to 11, and most preferably from pH 8 to 10, in particular from pH 9 to 10.

The bleaching composition of the present invention has particular application in detergent formulations, especially for laundry cleaning. Accordingly, in another preferred embodiment, the present invention provides a detergent bleach composition comprising a bleaching composition as defined above and additionally a surface-active material, optionally together with detergency builder.



- 16 -

The bleach composition according to the present invention may for example contain a surface-active material in an amount of from 10 to 50% by weight. The surface-active material may be naturally derived, such as soap, or a  
5 synthetic material selected from anionic, nonionic, amphoteric, zwitterionic, cationic actives and mixtures thereof. Many suitable actives are commercially available and are fully described in the literature, for example in "Surface Active Agents and Detergents", Volumes I and II, by  
10 Schwartz, Perry and Berch.

Typical synthetic anionic surface-actives are usually water-soluble alkali metal salts of organic sulfates and sulfonates having alkyl groups containing from about 8 to  
15 about 22 carbon atoms, the term "alkyl" being used to include the alkyl portion of higher aryl groups. Examples of suitable synthetic anionic detergent compounds are sodium and ammonium alkyl sulfates, especially those obtained by sulfating higher (C<sub>8</sub>-C<sub>18</sub>) alcohols produced, for example,  
20 from tallow or coconut oil; sodium and ammonium alkyl (C<sub>9</sub>-C<sub>20</sub>) benzene sulfonates, particularly sodium linear secondary alkyl (C<sub>10</sub>-C<sub>15</sub>) benzene sulfonates; sodium alkyl glyceryl ether sulfates, especially those ethers of the higher alcohols derived from tallow or coconut oil fatty acid  
25 monoglyceride sulfates and sulfonates; sodium and ammonium salts of sulfuric acid esters of higher (C<sub>9</sub>-C<sub>18</sub>) fatty alcohol alkylene oxide, particularly ethylene oxide, reaction products; the reaction products of fatty acids such as coconut fatty acids esterified with isethionic acid and  
30 neutralised with sodium hydroxide; sodium and ammonium salts of fatty acid amides of methyl taurine; alkane

- 17 -

monosulfonates such as those derived by reacting alpha-olefins (C<sub>8</sub>-C<sub>20</sub>) with sodium bisulfite and those derived by reacting paraffins with SO<sub>2</sub> and Cl<sub>2</sub> and then hydrolysing with a base to produce a random sulfonate; sodium and ammonium (C<sub>7</sub>-C<sub>12</sub>) dialkyl sulfosuccinates; and olefin sulfonates, which term is used to describe material made by reacting olefins, particularly (C<sub>10</sub>-C<sub>20</sub>) alpha-olefins, with SO<sub>3</sub> and then neutralising and hydrolysing the reaction product. The preferred anionic detergent compounds are sodium (C<sub>10</sub>-C<sub>15</sub>) alkylbenzene sulfonates, and sodium (C<sub>16</sub>-C<sub>18</sub>) alkyl ether sulfates.

Examples of suitable nonionic surface-active compounds which may be used, preferably together with the anionic surface-active compounds, include, in particular, the reaction products of alkylene oxides, usually ethylene oxide, with alkyl (C<sub>6</sub>-C<sub>22</sub>) phenols, generally 5-25 EO, i.e. 5-25 units of ethylene oxides per molecule; and the condensation products of aliphatic (C<sub>8</sub>-C<sub>18</sub>) primary or secondary linear or branched alcohols with ethylene oxide, generally 2-30 EO. Other so-called nonionic surface-actives include alkyl polyglycosides, sugar esters, long-chain tertiary amine oxides, long-chain tertiary phosphine oxides and dialkyl sulfoxides.

Amphoteric or zwitterionic surface-active compounds can also be used in the compositions of the invention but this is not normally desired owing to their relatively high cost. If any amphoteric or zwitterionic detergent compounds are used, it is generally in small amounts in compositions based on

- 18 -

the much more commonly used synthetic anionic and nonionic actives.

The detergent bleach composition of the invention will preferably comprise from 1 to 15 % wt of anionic surfactant and from 10 to 40 % by weight of nonionic surfactant. In a further preferred embodiment, the detergent active system is free from C<sub>16</sub>-C<sub>12</sub> fatty acid soaps.

10 The bleach composition of the present invention may also contains a detergency builder, for example in an amount of from about 5 to 80 % by weight, preferably from about 10 to 60 % by weight.

15 Builder materials may be selected from 1) calcium sequestrant materials, 2) precipitating materials, 3) calcium ion-exchange materials and 4) mixtures thereof.

Examples of calcium sequestrant builder materials include  
20 alkali metal polyphosphates, such as sodium tripolyphosphate; nitrilotriacetic acid and its water-soluble salts; the alkali metal salts of carboxymethyloxy succinic acid, ethylene diamine tetraacetic acid, oxydisuccinic acid, mellitic acid, benzene polycarboxylic  
25 acids, citric acid; and polyacetal carboxylates as disclosed in US-A-4,144,226 and US-A-4,146,495.

Examples of precipitating builder materials include sodium orthophosphate and sodium carbonate.

- 19 -

Examples of calcium ion-exchange builder materials include the various types of water-insoluble crystalline or amorphous aluminosilicates, of which zeolites are the best known representatives, e.g. zeolite A, zeolite B (also known  
5 as zeolite P), zeolite C, zeolite X, zeolite Y and also the zeolite P-type as described in EP-A-0,384,070.

In particular, the compositions of the invention may contain any one of the organic and inorganic builder materials,  
10 though, for environmental reasons, phosphate builders are preferably omitted or only used in very small amounts. Typical builders usable in the present invention are, for example, sodium carbonate, calcite/carbonate, the sodium salt of nitrilotriacetic acid, sodium citrate,  
15 carboxymethyloxy malonate, carboxymethyloxy succinate and water-insoluble crystalline or amorphous aluminosilicate builder materials, each of which can be used as the main builder, either alone or in admixture with minor amounts of other builders or polymers as co-builder.

20 It is preferred that the composition contains not more than 5% by weight of a carbonate builder, expressed as sodium carbonate, more preferably not more than 2.5 % by weight to substantially nil, if the composition pH lies in the lower  
25 alkaline region of up to 10.

Apart from the components already mentioned, the bleach composition of the present invention can contain any of the conventional additives in amounts of which such materials  
30 are normally employed in fabric washing detergent compositions. Examples of these additives include buffers

- 20 -

such as carbonates, lather boosters, such as alkanolamides, particularly the monoethanol amides derived from palmkernel fatty acids and coconut fatty acids; lather depressants, such as alkyl phosphates and silicones; anti-redeposition agents, such as sodium carboxymethyl cellulose and alkyl or substituted alkyl cellulose ethers; stabilisers, such as phosphonic acid derivatives (i.e. Dequest® types); fabric softening agents; inorganic salts and alkaline buffering agents, such as sodium sulfate and sodium silicate; and, usually in very small amounts, fluorescent agents; perfumes; enzymes, such as proteases, cellulases, lipases, amylases and oxidases; germicides and colourants.

Transition metal sequestrants such as EDTA, and phosphonic acid derivatives such as EDTMP (ethylene diamine tetra(methylene phosphonate)) may also be included, in addition to the ligand specified, for example to improve the stability sensitive ingredients such as enzymes, fluorescent agents and perfumes, but provided the composition remains bleaching effective. However, the composition according to the present invention containing the ligand, is preferably substantially, and more preferably completely, devoid of transition metal sequestrants (other than the ligand).

Whilst the present invention is based on the catalytic bleaching of a substrate by atmospheric oxygen or air, it will be appreciated that small amounts of hydrogen peroxide or peroxy-based or -generating systems may be included in the composition, if desired. Therefore, by "substantially devoid of peroxygen bleach or peroxy-based or -generating bleach systems" is meant that the composition contains from

- 21 -

0 to 50 %, preferably from 0 to 10 %, more preferably from 0 to 5 %, and optimally from 0 to 2 % by molar weight on an oxygen basis, of peroxygen bleach or peroxy-based or -generating bleach systems. Preferably, however, the composition will be wholly devoid of peroxygen bleach or peroxy-based or -generating bleach systems.

Thus, at least 10 %, preferably at least 50 % and optimally at least 90 % of any bleaching of the substrate is effected by oxygen sourced from the air.

According to the fourth aspect, the catalyst may be contacted to the textile fabric in any suitable manner. For example, it may be applied in dry form, such as in powder form, or in a liquor that is then dried, for example as an aqueous spray-on fabric treatment fluid or a wash liquor for laundry cleaning, or a non-aqueous dry cleaning fluid or spray-on aerosol fluid. Other suitable means of contacting the catalyst to the textile may be used, as further explained below.

Any suitable textile that is susceptible to bleaching or one that one might wish to subject to bleaching may be used. Preferably the textile is a laundry fabric or garment.

25

The bleaching method of the fourth aspect may be carried out by simply leaving the substrate in contact with the catalyst for a sufficient period of time. Preferably, however, the catalyst is in an aqueous medium, and the aqueous medium on or containing the substrate is agitated.

- 22 -

In a preferred embodiment, the treated textile is dried, by allowing it to dry under ambient temperature or at elevated temperatures.

5 In a particularly preferred embodiment the method according to the fourth aspect is carried out on a laundry fabric using aqueous treatment liquor. In particular the treatment may be effected in, or as an adjunct to, an essentially conventional wash cycle for cleaning laundry. More  
10 preferably, the treatment is carried out in an aqueous detergent wash liquor. The catalyst can be delivered into the wash liquor from a powder, granule, pellet, tablet, block, bar or other such solid form. The solid form can comprise a carrier, which can be particulate, sheet-like or  
15 comprise a three-dimensional object. The carrier can be dispersible or soluble in the wash liquor or may remain substantially intact. In other embodiments, the catalyst can be delivered into the wash liquor from a paste, gel or liquid concentrate.

20 It is particularly advantageous that the catalyst used in the method of the fourth aspect makes use of atmospheric oxygen in its bleaching activity. This avoids the requirement that peroxygen bleaches and/or other relatively  
25 large quantities of reactive substances need be used in the treatment process. Consequently, only a relatively small quantity of bleach active substance need be employed and this allows dosage routes to be exploited which could previously not be used. Thus, while it is preferable to  
30 include the catalyst in a composition that is normally used in a washing process, such as a pre-treatment, main-wash,

- 23 -

conditioning composition or ironing aid, other means for ensuring that the catalyst is present in the wash liquor may be envisaged.

5 For example, it is envisaged that the catalyst can be presented in the form of a body from which it is slowly released during the whole or part of the laundry process. Such release can occur over the course of a single wash or over the course of a plurality of washes. In the latter case  
10 it is envisaged that the catalyst can be released from a carrier substrate used in association with the wash process, e.g. from a body placed in the dispenser drawer of a washing machine, elsewhere in the delivery system or in the drum of the washing machine. When used in the drum of the washing  
15 machine the carrier can be freely moving or fixed relative to the drum. Such fixing can be achieved by mechanical means, for example by barbs that interact with the drum wall, or employ other forces, for example a magnetic force. The modification of a washing machine to provide for means  
20 to hold and retain such a carrier is envisaged similar means being known from the analogous art of toilet block manufacture. Freely moving carriers such as shuttles for dosage of surfactant materials and/or other detergent ingredients into the wash can comprise means for the release  
25 of the catalyst into the wash.

In the alternative, the catalyst can be presented in the form of a wash additive that preferably is soluble. The additive can take any of the physical forms used for wash  
30 additives, including powder, granule, pellet, sheet, tablet, block, bar or other such solid form or take the form of a



- 24 -

paste, gel or liquid. Dosage of the additive can be unitary or in a quantity determined by the user. While it is envisaged that such additives can be used in the main washing cycle, the use of them in the conditioning or drying  
5 cycle is not hereby excluded.

The present invention is not limited to those circumstances in which a washing machine is employed, but can be applied where washing is performed in some alternative vessel. In  
10 these circumstances it is envisaged that the catalyst can be delivered by means of slow release from the bowl, bucket or other vessel which is being employed, or from any implement which is being employed, such as a brush, bat or dolly, or from any suitable applicator.

15 Suitable pre-treatment means for application of the catalyst to the textile material prior to the main wash include sprays, pens, roller-ball devices, bars, soft solid applicator sticks and impregnated cloths or cloths  
20 containing microcapsules. Such means are well known in the analogous art of deodorant application and/or in spot treatment of textiles. Similar means for application are employed in those embodiments where the catalyst is applied after the main washing and/or conditioning steps have been  
25 performed, e.g. prior to or after ironing or drying of the cloth. For example, the catalyst may be applied using tapes, sheets or sticking plasters coated or impregnated with the substance, or containing microcapsules of the substance. The catalyst may for example be incorporated  
30 into a drier sheet so as to be activated or released during a tumble-drier cycle, or the substance can be provided in an

- 25 -

impregnated or microcapsule-containing sheet so as to be delivered to the textile when ironed.

Throughout the description and claims generic groups have been used, for example alkyl, alkoxy, aryl. Unless otherwise specified the following are preferred group restrictions that may be applied to generic groups found within compounds disclosed herein:

10 alkyl: linear and branched C1-C8-alkyl,

alkenyl: C2-C6-alkenyl,

cycloalkyl: C3-C8-cycloalkyl,

15

alkoxy: C1-C6-alkoxy,

alkylene: selected from the group consisting of: methylene; 1,1-ethylene; 1,2-ethylene; 1,1-propylidene; 1,2-propylene; 1,3-propylene; 2,2-propylidene; butan-2-ol-1,4-diyl; propan-2-ol-1,3-diyl; 1,4-butylene; cyclohexane-1,1-diyl; cyclohexan-1,2-diyl; cyclohexan-1,3-diyl; cyclohexan-1,4-diyl; cyclopentane-1,1-diyl; cyclopentan-1,2-diyl; and cyclopentan-1,3-diyl,

25

aryl: selected from homoaromatic compounds having a molecular weight under 300,

arylene: selected from the group consisting of: 1,2-phenylene; 1,3-phenylene; 1,4-phenylene; 1,2-naphtalenylene; 1,3-naphtalenylene; 1,4-naphtalenylene; 2,3-naphtalenylene;

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- 26 -

1-hydroxy-2,3-phenylene; 1-hydroxy-2,4-phenylene; 1-hydroxy-2,5-phenylene; and 1-hydroxy-2,6-phenylene,

heteroaryl: selected from the group consisting of:  
5 pyridinyl; pyrimidinyl; pyrazinyl; triazolyl; pyridazinyl;  
1,3,5-triazinyl; quinolinyl; isoquinolinyl; quinoxalinyl;  
imidazolyl; pyrazolyl; benzimidazolyl; thiazolyl;  
oxazolidinyl; pyrrolyl; carbazolyl; indolyl; and isoindolyl,  
wherein the heteroaryl may be connected to the compound via  
10 any atom in the ring of the selected heteroaryl,

heteroarylene: selected from the group consisting of:  
pyridindiyl; quinolindiyl; pyrazodiyl; pyrazoldiyl;  
triazolediyl; pyrazindiyl; and imidazolediyl, wherein the  
15 heteroarylene acts as a bridge in the compound via any atom  
in the ring of the selected heteroarylene, more specifically  
preferred are: pyridin-2,3-diyl; pyridin-2,4-diyl; pyridin-  
2,5-diyl; pyridin-2,6-diyl; pyridin-3,4-diyl; pyridin-3,5-  
diyl; quinolin-2,3-diyl; quinolin-2,4-diyl; quinolin-2,8-  
20 diyl; isoquinolin-1,3-diyl; isoquinolin-1,4-diyl; pyrazol-  
1,3-diyl; pyrazol-3,5-diyl; triazole-3,5-diyl; triazole-1,3-  
diyl; pyrazin-2,5-diyl; and imidazole-2,4-diyl,

heterocycloalkyl: selected from the group consisting of:  
25 pyrrolinyl; pyrrolidinyl; morpholinyl; piperidinyl;  
piperazinyl; hexamethylene imine; 1,4-piperazinyl;  
tetrahydrothiophenyl; tetrahydrofuranlyl; 1,4,7-  
triazacyclononanyl; 1,4,8,11-tetraazacyclotetradecanyl;  
1,4,7,10,13-pentaazacyclopentadecanyl; 1,4-diaza-7-thia-  
30 cyclononanyl; 1,4-diaza-7-oxa-cyclononanyl; 1,4,7,10-  
tetraazacyclododecanyl; 1,4-dioxanyl; 1,4,7-trithia-

- 27 -

cyclononanyl; tetrahydropyranyl; and oxazolidinyl, wherein the heterocycloalkyl may be connected to the compound via any atom in the ring of the selected heterocycloalkyl,

- 5 heterocycloalkylene: selected from the group consisting of:  
piperidin-1,2-ylene; piperidin-2,6-ylene; piperidin-4,4-  
ylidene; 1,4-piperazin-1,4-ylene; 1,4-piperazin-2,3-ylene;  
1,4-piperazin-2,5-ylene; 1,4-piperazin-2,6-ylene; 1,4-  
piperazin-1,2-ylene; 1,4-piperazin-1,3-ylene; 1,4-piperazin-  
10 1,4-ylene; tetrahydrothiophen-2,5-ylene; tetrahydrothiophen-  
3,4-ylene; tetrahydrothiophen-2,3-ylene; tetrahydrofuran-  
2,5-ylene; tetrahydrofuran-3,4-ylene; tetrahydrofuran-2,3-  
ylene; pyrrolidin-2,5-ylene; pyrrolidin-3,4-ylene;  
pyrrolidin-2,3-ylene; pyrrolidin-1,2-ylene; pyrrolidin-1,3-  
15 ylene; pyrrolidin-2,2-ylidene; 1,4,7-triazacyclonon-1,4-  
ylene; 1,4,7-triazacyclonon-2,3-ylene; 1,4,7-triazacyclonon-  
2,9-ylene; 1,4,7-triazacyclonon-3,8-ylene; 1,4,7-  
triazacyclonon-2,2-ylidene; 1,4,8,11-tetraazacyclotetradec-  
1,4-ylene; 1,4,8,11-tetraazacyclotetradec-1,8-ylene;  
20 1,4,8,11-tetraazacyclotetradec-2,3-ylene; 1,4,8,11-  
tetraazacyclotetradec-2,5-ylene; 1,4,8,11-  
tetraazacyclotetradec-1,2-ylene; 1,4,8,11-  
tetraazacyclotetradec-2,2-ylidene; 1,4,7,10-  
tetraazacyclododec-1,4-ylene; 1,4,7,10-tetraazacyclododec-  
25 1,7-ylene; 1,4,7,10-tetraazacyclododec-1,2-ylene; 1,4,7,10-  
tetraazacyclododec-2,3-ylene; 1,4,7,10-tetraazacyclododec-  
2,2-ylidene; 1,4,7,10,13-pentaazacyclopentadec-1,4-ylene;  
1,4,7,10,13-pentaazacyclopentadec-1,7-ylene; 1,4,7,10,13-  
pentaazacyclopentadec-2,3-ylene; 1,4,7,10,13-  
30 pentaazacyclopentadec-1,2-ylene; 1,4,7,10,13-  
pentaazacyclopentadec-2,2-ylidene; 1,4-diaza-7-thia-

- 28 -

cyclonon-1,4-ylene; 1,4-diaza-7-thia-cyclonon-1,2-ylene;  
1,4-diaza-7-thia-cyclonon-2,3-ylene; 1,4-diaza-7-thia-  
cyclonon-6,8-ylene; 1,4-diaza-7-thia-cyclonon-2,2-ylidene;  
1,4-diaza-7-oxa-cyclonon-1,4-ylene; 1,4-diaza-7-oxa-  
5 cyclonon-1,2-ylene; 1,4-diaza-7-oxa-cyclonon-2,3-ylene; 1,4-  
diaza-7-oxa-cyclonon-6,8-ylene; 1,4-diaza-7-oxa-cyclonon-  
2,2-ylidene; 1,4-dioxan-2,3-ylene; 1,4-dioxan-2,6-ylene;  
1,4-dioxan-2,2-ylidene; tetrahydropyran-2,3-ylene;  
tetrahydropyran-2,6-ylene; tetrahydropyran-2,5-ylene;  
10 tetrahydropyran-2,2-ylidene; 1,4,7-trithia-cyclonon-2,3-  
ylene; 1,4,7-trithia-cyclonon-2,9-ylene; and 1,4,7-trithia-  
cyclonon-2,2-ylidene,

amine: the group  $-N(R)_2$  wherein each R is independently  
15 selected from: hydrogen; C1-C6-alkyl; C1-C6-alkyl-C<sub>6</sub>H<sub>5</sub>; and  
phenyl, wherein when both R are C1-C6-alkyl both R together  
may form an -NC<sub>3</sub> to an -NC<sub>5</sub> heterocyclic ring with any  
remaining alkyl chain forming an alkyl substituent to the  
heterocyclic ring,

20

halogen: selected from the group consisting of: F; Cl; Br  
and I,

sulfonate: the group  $-S(O)_2OR$ , wherein R is selected  
25 from: hydrogen; C1-C6-alkyl; phenyl; C1-C6-alkyl-C<sub>6</sub>H<sub>5</sub>; Li;  
Na; K; Cs; Mg; and Ca,

sulfate: the group  $-OS(O)_2OR$ , wherein R is selected from:  
hydrogen; C1-C6-alkyl; phenyl; C1-C6-alkyl-C<sub>6</sub>H<sub>5</sub>; Li; Na; K;  
30 Cs; Mg; and Ca,

- 29 -

sulfone: the group  $-S(O)_2R$ , wherein R is selected from:  
hydrogen; C1-C6-alkyl; phenyl; C1-C6-alkyl-C<sub>6</sub>H<sub>5</sub> and amine  
(to give sulfonamide) selected from the group:  $-NR'_2$ ,  
wherein each R' is independently selected from: hydrogen;  
5 C1-C6-alkyl; C1-C6-alkyl-C<sub>6</sub>H<sub>5</sub>; and phenyl, wherein when both  
R' are C1-C6-alkyl both R' together may form an  $-NC_3$  to an  $-NC_5$  heterocyclic ring with any remaining alkyl chain forming  
an alkyl substituent to the heterocyclic ring,

10 carboxylate derivative: the group  $-C(O)OR$ , wherein R is  
selected from: hydrogen; C1-C6-alkyl; phenyl; C1-C6-alkyl-  
C<sub>6</sub>H<sub>5</sub>; Li; Na; K; Cs; Mg; and Ca,

carbonyl derivative: the group  $-C(O)R$ , wherein R is  
15 selected from: hydrogen; C1-C6-alkyl; phenyl; C1-C6-alkyl-  
C<sub>6</sub>H<sub>5</sub> and amine (to give amide) selected from the group:  $-NR'_2$ , wherein each R' is independently selected from:  
hydrogen; C1-C6-alkyl; C1-C6-alkyl-C<sub>6</sub>H<sub>5</sub>; and phenyl, wherein  
when both R' are C1-C6-alkyl both R' together may form an  $-NC_3$  to an  $-NC_5$  heterocyclic ring with any remaining alkyl  
20 chain forming an alkyl substituent to the heterocyclic ring,

phosphonate: the group  $-P(O)(OR)_2$ , wherein each R is  
independently selected from: hydrogen; C1-C6-alkyl; phenyl;  
25 C1-C6-alkyl-C<sub>6</sub>H<sub>5</sub>; Li; Na; K; Cs; Mg; and Ca,

phosphate: the group  $-OP(O)(OR)_2$ , wherein each R is  
independently selected from: hydrogen; C1-C6-alkyl; phenyl;  
C1-C6-alkyl-C<sub>6</sub>H<sub>5</sub>; Li; Na; K; Cs; Mg; and Ca,

- 30 -

phosphine: the group  $-P(R)_2$ , wherein each R is independently selected from: hydrogen; C1-C6-alkyl; phenyl; and C1-C6-alkyl-C<sub>6</sub>H<sub>5</sub>,

5 phosphine oxide: the group  $-P(O)R_2$ , wherein R is independently selected from: hydrogen; C1-C6-alkyl; phenyl; and C1-C6-alkyl-C<sub>6</sub>H<sub>5</sub>; and amine (to give phosphonamidate) selected from the group:  $-NR'_2$ , wherein each R' is independently selected from: hydrogen; C1-C6-alkyl; C1-C6-  
10 alkyl-C<sub>6</sub>H<sub>5</sub>; and phenyl, wherein when both R' are C1-C6-alkyl both R' together may form an -NC<sub>3</sub> to an -NC<sub>5</sub> heterocyclic ring with any remaining alkyl chain forming an alkyl substituent to the heterocyclic ring.

15 Unless otherwise specified the following are more preferred group restrictions that may be applied to groups found within compounds disclosed herein:

alkyl: linear and branched C1-C6-alkyl,

20

alkenyl: C3-C6-alkenyl,

cycloalkyl: C6-C8-cycloalkyl,

25 alkoxy: C1-C4-alkoxy,

alkylene: selected from the group consisting of: methylene; 1,2-ethylene; 1,3-propylene; butan-2-ol-1,4-diyl; 1,4-butylene; cyclohexane-1,1-diyl; cyclohexan-1,2-diyl;  
30 cyclohexan-1,4-diyl; cyclopentane-1,1-diyl; and cyclopentan-1,2-diyl,

- 31 -

aryl: selected from group consisting of: phenyl;  
biphenyl; naphthalenyl; anthracenyl; and phenanthrenyl,

5 arylene: selected from the group consisting of: 1,2-phenylene; 1,3-phenylene; 1,4-phenylene; 1,2-naphthalenylene; 1,4-naphthalenylene; 2,3-naphthalenylene and 1-hydroxy-2,6-phenylene,

10 heteroaryl: selected from the group consisting of: pyridinyl; pyrimidinyl; quinolinyl; pyrazolyl; triazolyl; isoquinolinyl; imidazolyl; and oxazolidinyl, wherein the heteroaryl may be connected to the compound via any atom in the ring of the selected heteroaryl,

15 heteroarylene: selected from the group consisting of: pyridin-2,3-diyl; pyridin-2,4-diyl; pyridin-2,6-diyl; pyridin-3,5-diyl; quinolin-2,3-diyl; quinolin-2,4-diyl; isoquinolin-1,3-diyl; isoquinolin-1,4-diyl; pyrazol-3,5-  
20 diyl; and imidazole-2,4-diyl,

heterocycloalkyl: selected from the group consisting of: pyrrolidinyl; morpholinyl; piperidinyl; piperidinyl; 1,4-piperazinyl; tetrahydrofuranlyl; 1,4,7-triazacyclononanyl;  
25 1,4,8,11-tetraazacyclotetradecanyl; 1,4,7,10,13-pentaazacyclopentadecanyl; 1,4,7,10-tetraazacyclododecanyl; and piperazinyl, wherein the heterocycloalkyl may be connected to the compound via any atom in the ring of the selected heterocycloalkyl,

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- 32 -

heterocycloalkylene: selected from the group consisting of: piperidin-2,6-ylene; piperidin-4,4-ylidene; 1,4-piperazin-1,4-ylene; 1,4-piperazin-2,3-ylene; 1,4-piperazin-2,6-ylene; tetrahydrothiophen-2,5-ylene; tetrahydrothiophen-3,4-ylene; tetrahydrofuran-2,5-ylene; tetrahydrofuran-3,4-ylene; pyrrolidin-2,5-ylene; pyrrolidin-2,2-ylidene; 1,4,7-triazacyclonon-1,4-ylene; 1,4,7-triazacyclonon-2,3-ylene; 1,4,7-triazacyclonon-2,2-ylidene; 1,4,8,11-tetraazacyclotetradec-1,4-ylene; 1,4,8,11-tetraazacyclotetradec-1,8-ylene; 1,4,8,11-tetraazacyclotetradec-2,3-ylene; 1,4,8,11-tetraazacyclotetradec-2,2-ylidene; 1,4,7,10-tetraazacyclododec-1,4-ylene; 1,4,7,10-tetraazacyclododec-1,7-ylene; 1,4,7,10-tetraazacyclododec-2,3-ylene; 1,4,7,10-tetraazacyclododec-2,2-ylidene; 1,4,7,10,13-pentaazacyclopentadec-1,4-ylene; 1,4,7,10,13-pentaazacyclopentadec-1,7-ylene; 1,4-diaza-7-thia-cyclonon-1,4-ylene; 1,4-diaza-7-thia-cyclonon-2,3-ylene; 1,4-diaza-7-thia-cyclonon-2,2-ylidene; 1,4-diaza-7-oxa-cyclonon-1,4-ylene; 1,4-diaza-7-oxa-cyclonon-2,3-ylene; 1,4-diaza-7-oxa-cyclonon-2,2-ylidene; 1,4-dioxan-2,6-ylene; 1,4-dioxan-2,2-ylidene; tetrahydropyran-2,6-ylene; tetrahydropyran-2,5-ylene; and tetrahydropyran-2,2-ylidene,

25

amine: the group  $-N(R)_2$ , wherein each R is independently selected from: hydrogen; C1-C6-alkyl; and benzyl,

halogen: selected from the group consisting of: F and Cl,

30

- 33 -

sulfonate: the group  $-S(O)_2OR$ , wherein R is selected from: hydrogen; C1-C6-alkyl; Na; K; Mg; and Ca,

5 sulfate: the group  $-OS(O)_2OR$ , wherein R is selected from: hydrogen; C1-C6-alkyl; Na; K; Mg; and Ca,

sulfone: the group  $-S(O)_2R$ , wherein R is selected from: hydrogen; C1-C6-alkyl; benzyl and amine selected from the group:  $-NR'_2$ , wherein each R' is independently selected  
10 from: hydrogen; C1-C6-alkyl; and benzyl,

carboxylate derivative: the group  $-C(O)OR$ , wherein R is selected from hydrogen; Na; K; Mg; Ca; C1-C6-alkyl; and benzyl,

15 carbonyl derivative: the group:  $-C(O)R$ , wherein R is selected from: hydrogen; C1-C6-alkyl; benzyl and amine selected from the group:  $-NR'_2$ , wherein each R' is independently selected from: hydrogen; C1-C6-alkyl; and  
20 benzyl,

phosphonate: the group  $-P(O)(OR)_2$ , wherein each R is independently selected from: hydrogen; C1-C6-alkyl; benzyl; Na; K; Mg; and Ca,

25 phosphate: the group  $-OP(O)(OR)_2$ , wherein each R is independently selected from: hydrogen; C1-C6-alkyl; benzyl; Na; K; Mg; and Ca,

- 34 -

phosphine: the group  $-P(R)_2$ , wherein each R is independently selected from: hydrogen; C1-C6-alkyl; and benzyl,

- 5 phosphine oxide: the group  $-P(O)R_2$ , wherein R is independently selected from: hydrogen; C1-C6-alkyl; benzyl and amine selected from the group:  $-NR'_2$ , wherein each R' is independently selected from: hydrogen; C1-C6-alkyl; and benzyl.

10

The invention will now be further illustrated by way of the following non-limiting examples:

#### EXAMPLES

15

Compound 1-7 were tested for catalytic bleaching activity using air.

Compound 1:  $[\{(TPA)Fe(H_2O)\}_2(\mu-O)](ClO_4)_4$

20 TPA=tris(pyridin-2-ylmethyl)amine.

Compound 2: tris(3-methyl-pyridin-2-ylmethyl)amine +  $Mn(ClO_4)_2 \cdot 6H_2O$

Compound 3: tris(3-methyl-pyridin-2-ylmethyl)amine +  $Fe(ClO_4)_2 \cdot 6H_2O$

25 Compound 4: tris(4-methyl-pyridin-2-ylmethyl)amine +  $Fe(ClO_4)_2 \cdot 6H_2O$

Compound 5: tris(5-methyl-pyridin-2-ylmethyl)amine

Compound 6: tris(5-methyl-pyridin-2-ylmethyl)amine +  $Mn(ClO_4)_2 \cdot 6H_2O$

30

- 35 -

Compound 7: tris(5-methyl-pyridin-2-ylmethyl)amine +  
Fe(ClO<sub>4</sub>)<sub>2</sub> · 6H<sub>2</sub>O

Compound 8: tris(4-t-butyl-pyridin-2-ylmethyl)amine +  
Fe(ClO<sub>4</sub>)<sub>2</sub> · 6H<sub>2</sub>O

5 Compound 9: tris(4-t-butyl-pyridin-2-ylmethyl)amine +  
Mn(ClO<sub>4</sub>)<sub>2</sub> · 6H<sub>2</sub>O

Compound 10: tris((4-t-butyl)-pyridin-2-ylmethyl)amine +  
Co(ClO<sub>4</sub>)<sub>2</sub> · 6H<sub>2</sub>O

10 Compound 1 was kindly donated by prof. L. Que, University of  
Minnesota, USA.

Tris(3-methyl-pyridin-2-ylmethyl)amine and Tris(5-methyl-  
pyridin-2-ylmethyl)amine

were synthesised according to the literature (E.C.

15 Wilkinson, et al., J. Am. Chem. Soc., 120, 955 (1998) and  
Y. Dong et al, J. Am. Chem. Soc., 117,, 2778 (1995)  
respectively.

**Synthesis of tris((4-t-butyl)-pyridin-2-ylmethyl)amine**

20 4-t-butyl-2-picoline (1a): In a two-neck round bottom flask,  
30.39 g (226 mmol) of 4-t-butyl pyridine was dissolved in  
freshly distilled diethylether (250 ml) and deoxygenated by  
bubbling with Ar. Into an addition funnel was added 162 ml  
(227 mmol) of MeLi under Ar. This was very slowly (dropwise)  
25 introduced into the stirring solution of 4-t-butyl-2-  
pyridine at -78°C. The solution was stirred for 2 hrs,  
warmed to room temperature, whereupon its color changed to  
pale orange. Stirring overnight resulted in a change of the  
solution to a bright red color. Distilled H<sub>2</sub>O was added  
30 dropwise until no evolution of gas was observed. The  
reaction mixture was filtered to remove LiOH and the

- 36 -

filtrate was collected. The filtered solid was washed with ether and the ether solution was combined with the previous filtrate. The solvent was removed by rotary evaporation to give a yellow oil (32.6 g). Distillation under vacuum gave  
5 24.3 g of a pale yellow oil product..

*4-t-butyl-2-picoline N-oxide (1b)*: To a mixture of 4-t-butyl-2-picoline (24.3 g) and glacial acetic acid (100 ml) was added 20 ml of H<sub>2</sub>O<sub>2</sub> (30%). This mixture was stirred at  
10 80°C for 12 hrs. Addition of another 20 ml of H<sub>2</sub>O<sub>2</sub> was followed by further stirring at 80°C (12 hrs). The resulting mixture was cooled to room temperature and the volatile components were removed on a high-vacuum rotavap to give a pale orange oil. This was dissolved in 100 ml CHCl<sub>3</sub> and  
15 stirred over Na<sub>2</sub>CO<sub>3</sub> for 2 hrs. Filtration into a 500 ml round bottom flask, followed by rotary evaporation give 22 g of a thick pale orange oil.

*2-acethoxymethyl-4-t-butyl-pyridine (1c)*: In a 500 ml round  
20 bottom flask, 22 g of 4-t-butyl-2-picoline N-oxide was mixed with 100 ml acetic anhydrid. After refluxing for 8 hrs, the mixture was cooled to room temperature and the volatiles removed on a high-vacuum rotavap, yielding a dark brown oil. Distillation under vacuum gave a pale yellow liquid (9.1 g;  
25 20%).

*2-hydroxymethyl-4-t-butyl-pyridine (1d)*: In a 250 ml round bottom flask, 5 g of NaOH was dissolved in 50 ml of distilled water, 9 g of 2-acethoxymethyl-4-t-butyl-pyridine  
30 was added, and the mixture was refluxed for 30 hrs. After cooling and extraction with diethylether, the organic layer

- 37 -

was dried ( $\text{Na}_2\text{SO}_4$ ), filtered and solvent removed to give an orange oil (7.0 g; 98%).

2-chloromethyl-4-t-butyl-pyridine (1e): In a 250 ml round  
5 bottom flask, 7.0 g of 2-hydroxymethyl-4-t-butyl-pyridine  
was dissolved in 50 ml  $\text{CH}_2\text{Cl}_2$ . A solution of freshly  
distilled thionyl chloride (4.0 g, 33.6 mmol) in 50 ml  $\text{CH}_2\text{Cl}_2$   
was added dropwise. The reaction mixture was stirred at room  
temperature for 2 hrs. The solution was made basic using  
10 with saturated  $\text{Na}_2\text{CO}_3(\text{aq})$ . The organic layer was separated  
and the aqueous layer was extracted with  $\text{CH}_2\text{Cl}_2$ . The combined  
organic layers were dried over  $\text{Na}_2\text{SO}_4$ . The volatile  
components were removed and the crude oil was distilled to  
give a pale yellow oil.

15

2-phthalimido-4-t-butyl-pyridine (1f): To a stirred solution  
of 2-chloromethyl-4-t-butyl-pyridine (2.0 g, 0.0109 mol) in  
DMF (20 ml) was added 2.47 g (0.0133 mol) of potassium  
phthalimide. The reaction mixture was stirred at 85 °C for  
20 25 hrs. The reaction mixture was cooled to room temperature  
and the volatile components were removed under reduced  
pressure. The remaining solid residue was dissolved in 100  
ml of water and the aqueous solution was extracted with  
 $\text{CH}_2\text{Cl}_2$ . The combined organic layers were dried over  $\text{Na}_2\text{SO}_4$ .  
25 The volatile components were removed leaving a solid residue  
which was recrystallized from hot EtOH to give 2.6 g of a  
crystalline solid. (81%).

2-aminoethyl-4-t-butyl-pyridine • 2HCl (1g): In a 100 ml  
30 round bottom flask equipped with a stir bar, 2-phthalimido-  
4-t-butyl-pyridine (2.4 g, 8.15 mmol) was dissolved in a

- 38 -

mixture of HCl (12N, 10ml) and glacial acetic acid (10 ml). The pale yellow solution was refluxed for 48 hrs and during this interval 3 aliquots (3 ml each of concentrated HCl) were introduced. The reaction mixture was cooled and the  
5 volatile components were removed under reduced pressure.

*Tris[(((4-t-butyl)-pyridin-2-yl)methyl)amine*: To a stirred solution of 2-aminomethyl-4-t-butyl-pyridine • 2HCl (1.18 g, 5.0 mmol) in water (10 ml), 2.35 g (10 mmol) of 2-  
10 chloromethyl-4-t-butyl-pyridine was added. A solution of NaOH (1.2 g, 30 mmol) in 4 ml of water was added at 0 °C. The reaction mixture was allowed to stir at room temperature for 12 hrs (whereupon the pH of the solution dropped to 7.0). The reaction mixture was filtered using a coarse frit  
15 and washed with water, and dried in vacuo, yielding 2.04 g of a white solid (89%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 8.42 (d, 3H, J = 6.0 Hz), 7.82 (s, 3H), 7.12 (d, 3H, J = 3.0 Hz), 3.89 (s, 6H), 1.29 (s, 27H).

## 20 Experimental:

In an aqueous solution containing 10 mM carbonate buffer (pH 10) without and with 0.6 g/l NaLAS (linear alkylbenzene sulfonate) or containing 10 mM borate buffer (pH 8) without  
25 and with 0.6 g/l NaLAS, tomato-soya oil stained cloths were added and kept in contact with the solution under agitation for 30 minutes at 30 °C. In comparative experiments, the same experiments were done by addition of 10 µM of compound 1, or 10 µM of transition-metal salt in combination with 20 µM  
30 ligand (compounds 2-7) referred to in the table below.

After the wash, the cloths were rinsed with water and subsequently dried at 30 °C and the change in colour was measured immediately after drying with a Linotype-Hell scanner (ex Linotype) ("t=0" in table 1) and after 1 day  
5 storage in the dark ("t=1" in table 1). The change in colour (including bleaching) is expressed as the  $\Delta E$  value. The measured colour difference ( $\Delta E$ ) between the washed cloth and the unwashed cloth is defined as follows:

10 
$$\Delta E = [(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2]^{1/2}$$

wherein  $\Delta L$  is a measure for the difference in darkness between the washed and unwashed test cloth;  $\Delta a$  and  $\Delta b$  are measures for the difference in redness and yellowness  
15 respectively between both cloths. With regard to this colour measurement technique, reference is made to Commission International de l'Eclairage (CIE); Recommendation on Uniform Colour Spaces, colour difference equations, psychometric colour terms, supplement no 2 to CIE  
20 Publication, no 15, Colorimetry, Bureau Central de la CIE, Paris 1978. The results are shown below in Tables 1 and 2:



- 40 -

Table 1

Results on tomato oil stains

	pH 8 - LAS	pH 8 + LAS	pH 10 - LAS	pH 10 + LAS
	t=0 t=1	t=0 t=1	t=0 t=1	t=0 t=1
Blank	1 2	2 3	1 2	3 4
Compound 1	1 2	4 6	1 1	3 4
Compound 2	2 2	4 8	4 16	6 18
Compound 5	2 2	5 6	4 4	7 8
Compound 6	2 2	4 14	14 18	7 18
Compound 8	3 5	3 4	3 3	6 7
Compound 9	2 3	4 4	3 11	5 15
Compound 10	4 8	3 4	7 13	6 8

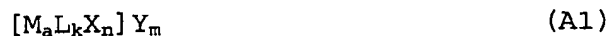
Table 2

Results on Curry Oil stains

	pH 8 - LAS	pH 8 + LAS	pH 10 - LAS	PH 10 + LAS
	t=0 t=1	t=0 t=1	t=0 t=1	t=0 t=1
Blank	3 4	3 3	12 12	13 13
Compound 3	6 8	7 7	17 17	17 17
Compound 4	5 7	7 7	17 17	15 15
Compound 6	5 5	6 6	17 16	15 15
Compound 7	8 9	8 8	16 15	16 15
Compound 8	8 9	8 8	14 14	17 15

CLAIMS:

1. A bleaching composition comprising, in an aqueous medium, atmospheric oxygen and a ligand which forms a complex with a transition metal, the complex catalysing bleaching of a substrate by the atmospheric oxygen, wherein the aqueous medium is substantially devoid of peroxygen bleach or a peroxy-based or -generating bleach system, wherein the ligand forms a complex of the general formula (A1):



in which:

- M represents a metal selected from Mn(II)-(III)-(IV)-(V), Cu(I)-(II)-(III), Fe(II)-(III)-(IV)-(V), Co(I)-(II)-(III), Ti(II)-(III)-(IV), V(II)-(III)-(IV)-(V), Mo(II)-(III)-(IV)-(V)-(VI) and W(IV)-(V)-(VI);

- X represents a coordinating species selected from any mono, bi or tri charged anions and any neutral molecules able to coordinate the metal in a mono, bi or tridentate manner;

Y represents any non-coordinated counter ion;

a represents an integer from 1 to 10;

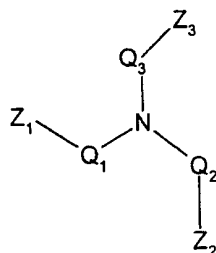
- k represents an integer from 1 to 10;

n represents an integer from 1 to 10;

m represents zero or an integer from 1 to 20; and

L represents a ligand of the general formula (I), or its protonated or deprotonated analogue:

- 43 -



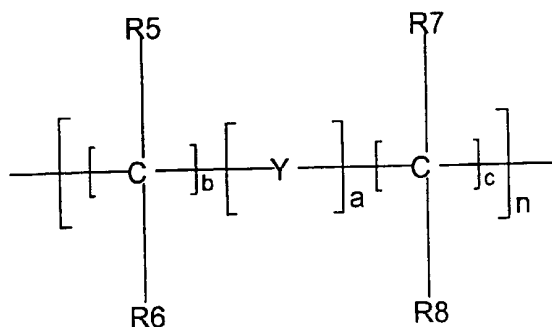
(I)

wherein

5  $Z_1$ ,  $Z_2$  and  $Z_3$  independently represent a coordinating group selected from carboxylate, amido,  $-NH-C(NH)NH_2$ , hydroxyphenyl, an optionally substituted heterocyclic ring or an optionally substituted heteroaromatic ring selected from pyridine, pyrimidine, pyrazine, pyrazole, imidazole, benzimidazole, quinoline, quinoxaline, triazole, isoquinoline, carbazole, indole, isoindole, oxazole and thiazole;

$Q_1$ ,  $Q_2$ , and  $Q_3$  independently represent a group of the formula:

15



wherein

20  $5 \geq a+b+c \geq 1$ ;  $a=0-5$ ;  $b=0-5$ ;  $c=0-5$ ;  $n=1$  or  $2$ ;

- 44 -

Y independently represents a group selected from -O-, -S-, -SO-, -SO<sub>2</sub>-, -C(O)-, arylene, alkylene, heteroarylene, heterocycloalkylene, -(G)P-, -P(O)- and -(G)N-, wherein G is selected from hydrogen, alkyl, aryl, arylalkyl, cycloalkyl, each except hydrogen being optionally substituted by one or more functional groups E;

R<sub>5</sub>, R<sub>6</sub>, R<sub>7</sub>, R<sub>8</sub> independently represent a group selected from hydrogen, hydroxyl, halogen, -R and -OR, wherein R represents alkyl, alkenyl, cycloalkyl, heterocycloalkyl, aryl, heteroaryl or a carbonyl derivative group, R being optionally substituted by one or more functional groups E, or R<sub>5</sub> together with R<sub>6</sub>, or R<sub>7</sub> together with R<sub>8</sub>, or both, represent oxygen, or R<sub>5</sub> together with R<sub>7</sub> and/or independently R<sub>6</sub> together with R<sub>8</sub>, or R<sub>5</sub> together with R<sub>8</sub> and/or independently R<sub>6</sub> together with R<sub>7</sub>, represent C<sub>1-6</sub>-alkylene optionally substituted by C<sub>1-4</sub>-alkyl, -F, -Cl, -Br or -I; and

E independently represents a functional group selected from -F, -Cl, -Br, -I, -OH, -OR', -NH<sub>2</sub>, -NHR', -N(R')<sub>2</sub>, -N(R')<sub>3</sub><sup>+</sup>, -C(O)R', -OC(O)R', -COOH, -COO<sup>-</sup>(Na<sup>+</sup>, K<sup>+</sup>), -COOR', -C(O)NH<sub>2</sub>, -C(O)NHR', -C(O)N(R')<sub>2</sub>, heteroaryl, -R', -SR', -SH, -P(R')<sub>2</sub>, -P(O)(R')<sub>2</sub>, -P(O)(OH)<sub>2</sub>, -P(O)(OR')<sub>2</sub>, -NO<sub>2</sub>, -SO<sub>3</sub>H, -SO<sub>3</sub><sup>-</sup>(Na<sup>+</sup>, K<sup>+</sup>), -S(O)<sub>2</sub>R', -NHC(O)R', and -N(R')C(O)R', wherein R' represents cycloalkyl, aryl, arylalkyl, or alkyl optionally substituted by -F, -Cl, -Br, -I, -NH<sub>3</sub><sup>+</sup>, -SO<sub>3</sub>H, -SO<sub>3</sub><sup>-</sup>(Na<sup>+</sup>, K<sup>+</sup>), -COOH, -COO<sup>-</sup>(Na<sup>+</sup>, K<sup>+</sup>), -P(O)(OH)<sub>2</sub>, or -P(O)(O<sup>-</sup>(Na<sup>+</sup>, K<sup>+</sup>))<sub>2</sub>.

- 45 -

2. A bleaching composition according to claim 1, wherein the medium has a pH value in the range from pH 6 to 11, preferably in the range from pH 8 to 10.

5 3. A bleaching composition according to claim 1 or claim 2, wherein the medium is substantially devoid of a transition metal sequestrant.

10 4. A bleaching composition according to any of claims 1 to 3, wherein the composition comprises a preformed complex of the ligand and a transition metal.

15 5. A bleaching composition according to any of claims 1 to 3, wherein the ligand is present as a free ligand that complexes with a transition metal present in the water.

20 6. A bleaching composition according to any of claims 1 to 3, wherein the ligand is present as a free ligand that complexes with a transition metal present in the substrate.

7. A bleaching composition according to any of claims 1 to 3, wherein the composition comprises the ligand present as a free ligand or a transition metal-substitutable metal-ligand complex, and a source of transition metal.

25 8. A bleaching composition according to any preceding claim, wherein  $Z_1$ ,  $Z_2$  and  $Z_3$  independently represent a coordinating group selected from optionally substituted pyridin-2-yl, optionally substituted imidazol-2-yl, 30 optionally substituted imidazol-4-yl, optionally substituted pyrazol-1-yl, and optionally substituted quinolin-2-yl.

- 46 -

9. A bleaching composition according to any preceding claim, wherein  $Z_1$ ,  $Z_2$  and  $Z_3$  each represent optionally substituted pyridin-2-yl.

5 10. A bleaching composition according to claim 8 or claim 9, wherein  $Z_1$ ,  $Z_2$  and  $Z_3$  are each substituted by a group selected from  $C_{1-4}$ -alkyl, aryl, arylalkyl, heteroaryl, methoxy, hydroxy, nitro, amino, carboxyl, halo, and carbonyl.

10

11. A bleaching composition according to claim 10, wherein  $Z_1$ ,  $Z_2$  and  $Z_3$  are each substituted by a methyl group.

12. A bleaching composition according to any preceding  
15 claim, wherein  $R_5$ ,  $R_6$ ,  $R_7$ ,  $R_8$  independently represent a group selected from -H, -hydroxy- $C_0$ - $C_{20}$ -alkyl, halo- $C_0$ - $C_{20}$ -alkyl, nitroso, formyl- $C_0$ - $C_{20}$ -alkyl, carboxyl- $C_0$ - $C_{20}$ -alkyl and esters and salts thereof, carbamoyl- $C_0$ - $C_{20}$ -alkyl, sulfo- $C_0$ - $C_{20}$ -alkyl and esters and salts thereof, sulfamoyl- $C_0$ - $C_{20}$ -  
20 alkyl, amino- $C_0$ - $C_{20}$ -alkyl, aryl- $C_0$ - $C_{20}$ -alkyl,  $C_0$ - $C_{20}$ -alkyl, alkoxy- $C_0$ - $C_6$ -alkyl, carbonyl- $C_0$ - $C_6$ -alkoxy, and  $C_0$ - $C_{20}$ -alkylamide.

13. A bleaching composition according to any preceding  
25 claim, wherein  $Q_1$ ,  $Q_2$  and  $Q_3$  are defined such that  $a=b=0$ ,  $c=1$  or 2, and  $n=1$ .

14. A bleaching composition according to any preceding  
claim, wherein  $Q_1$ ,  $Q_2$  and  $Q_3$  independently represent a group  
30 selected from  $-CH_2-$  and  $-CH_2CH_2-$ .

- 47 -

15. A bleaching composition according to claim 1, wherein the ligand L is selected from tris(pyridin-2-ylmethyl)amine, tris(3-methyl-pyridin-2-ylmethyl)amine, tris(5-methyl-pyridin-2-ylmethyl)amine, tris(4-t-butyl-pyridin-2-ylmethyl)amine and  
5 tris(6-methyl-pyridin-2-ylmethyl)amine.

16. A bleaching composition according to any preceding claim, wherein the composition comprises a mixture of the ligand L and a metal salt  $MX_n$  in which  $n=1-5$ , preferably 1-3.

10

17. A method of bleaching a substrate comprising applying to the substrate, in an aqueous medium, a ligand which forms a complex with a transition metal, the complex catalysing bleaching of the substrate by atmospheric oxygen, wherein  
15 the ligand is as defined in any of claims 1 to 15.

18. A method according to claim 17, wherein the majority of the bleaching species in the medium (on an equivalent weight basis) is derived from the atmospheric oxygen.

20

19. A method according to claim 19 or claim 20, wherein the medium is substantially devoid of peroxygen bleach or a peroxy-based or -generating bleach system.

25 20. Use of a ligand which forms a complex with a transition metal as a catalytic bleaching agent for a substrate in an aqueous medium substantially devoid of peroxygen bleach or a peroxy-based or -generating bleach system, the complex catalysing bleaching of the substrate by the atmospheric  
30 oxygen wherein the ligand is as defined in any of claims 1 to 17.



- 48 -

21. A method of treating a textile by contacting the textile with a ligand which forms a complex with a transition metal, whereby the complex catalyses bleaching of the textile by atmospheric oxygen after the treatment,  
5 wherein the ligand is as defined in any of claims 1 to 15.

22. A ligand as defined in claim 10 or claim 11.

23. The ligand tris(4-t-butyl-pyridin-2-ylmethyl)amine.

10

24. A complex comprising a ligand as defined in claim 22 or claim 23.

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WO 01/16261 A3

(54) Title: COMPOSITION AND METHOD FOR BLEACHING A SUBSTRATE

(57) Abstract: The invention relates a method of bleaching a substrate that comprises applying to a substrate, in an aqueous medium, a specified ligand which forms a complex with a transition metal, the complex catalysing bleaching of the substrate by atmospheric oxygen. Also provided in an aqueous bleaching composition substantially devoid of peroxygen bleach or a peroxy-based or generating bleach system. Also provided is a method of treating a textile such as a laundry fabric whereby a complex catalyses bleaching of the textile by atmospheric oxygen after the treatment. The catalyst may be used in dry form, or in a liquor that is then dried, such as an aqueous spray-on fabric treatment fluid or a wash liquor for laundry cleaning, or a non-aqueous dry cleaning fluid or spray-on aerosol fluid.

# INTERNATIONAL SEARCH REPORT

Internatic Application No

PCT/EP 00/08078

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C11D3/39 D06L3/02 C07D213/36 .

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C11D D06L C07D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DONG Y ET AL: "A HIGH-VALENT NONHEME IRON INTERMEDIATE. STRUCTURE AND PROPERTIES OF (Fe <sub>2</sub> (MU-O) <sub>2</sub> (5-Me-TPA) <sub>2</sub> (C <sub>10</sub> A) <sub>3</sub> " JOURNAL OF THE AMERICAN CHEMICAL SOCIETY, US, AMERICAN CHEMICAL SOCIETY, WASHINGTON, DC, vol. 117, 1995, pages 2778-2792, XP002040679 ISSN: 0002-7863 cited in the application scheme 1	22,24
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Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

### \* Special categories of cited documents:

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- \*O\* document referring to an oral disclosure, use, exhibition or other means
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- \* & \* document member of the same patent family

Date of the actual completion of the international search

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# INTERNATIONAL SEARCH REPORT

Internatic Application No  
PCT/EP 00/08078

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	ZANG Y ET AL: "MODELS FOR NONHEME IRON INTERMEDIATES: STRUCTURAL BASIS FOR TUNING THE SPIN STATES OF Fe(TPA) COMPLEXES" JOURNAL OF THE AMERICAN CHEMICAL SOCIETY, US, AMERICAN CHEMICAL SOCIETY, WASHINGTON, DC, vol. 119, 7 May 1997 (1997-05-07), pages 4197-4205, XP002040680 ISSN: 0002-7863	22, 24
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